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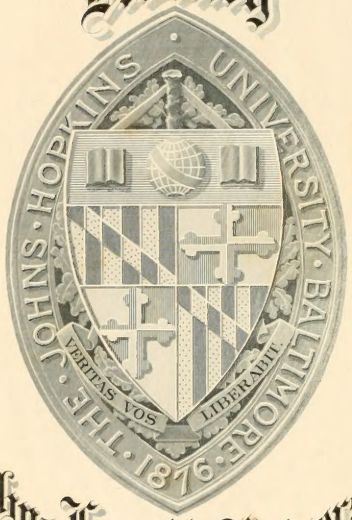

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A Study of the Action of the Nitrate and Sulphate of Para-Diazo-Toluene on Methyl Alcohol Under Various Conditions.

Dissertation

Submitted to the Board of University Studies of the Johns Hopkins University, for the Degree of Doctor of Philosophy

by

William E. Chamberlin.

1894.

J. H.

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Acknowledgment.

The work described in this thesis was undertaken at the suggestion of Professor Remsen, who has directed my research in the Chemical Laboratory of The Johns Hopkins University during the scholastic year 1893-4.

To Professor Remsen, as well as to Professors H. N. Morse, Geo. H. Williams, and J. S. Ames, the writer would here express his gratitude for valuable instruction and assistance rendered freely.

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The action of Nitrites and Para-Diazo-Toluene upon Methyl Alcohol.

Introduction.

In the study of the action of alcohols upon diazo-compounds many facts of interest have been brought to light. It was long supposed that the only action of an alcohol upon a diazo-salt was to substitute hydrogen for the diazo-group. Many investigators have shown, however, that the normal action of an alcohol is rather to substitute an alkoxy-group for the diazo-group of the diazo salt.

Remsen and Orndorff[1] found that, when ethyl alcohol acts upon para-diazo-toluene sulphate, both ethoxy-toluene and toluene are formed, the latter in [illegible] quantity.

[1] Am. Ch. J. I. 376.

Lachowicz and myself have proven the presence of hydrazines and hydrazoic acid in the products of the reduction, and that the diminution of hydrazine and hydrazoic acid leads to form the hydrazoic reaction.

Bamberger[1] found that, when diazo-benzene nitrate and acetate are boiled with water in the presence of alkalies or of zinc dust, then neutralizing the acid liberated in the decomposition, the hydrazoic reaction takes place exclusively, and not the azoxy reaction as was supposed.

These facts made it of interest to study more thoroughly the reaction of the salts of the nitro-bases with alcohols. The present paper contains a description of the action of para-diazotoluene nitrate and sulphate when boiled with alcohols under various conditions. It is also intended to describe, together with a study of the products of reduction, especially, the hydrazine, its

[1] Am. Ch. J. 15, 124. [2] Dissertation, 1893.; Am. Ch. Jr. 16. 244.

carbonate, zinc dust, and zinc oxide, which the course of the reaction.

Preparation of Para-Diazo-Toluene Nitrate.

The method of preparing the nitrate which was found to work best is as follows: 40 grams of pure para-toluidine are placed in a beaker of 450 c.c. capacity, and 40 grams of pure concentrated nitric acid diluted with an equal bulk of water, is added to the toluidine. The nitric is then stirred until a uniform mixture is obtained, and the toluidine nitrate forms a crystalline mass. The beaker is then placed in cold water, and the contents stirred vigorously, so that the crystals may be as small as possible. When the mass is cold it is drained, the mother liquor is put aside, and the crystals washed with a little water. After draining as

completely as possible. The crystals of toluidine nitrate are dried upon a porous plate and powdered. The salt is then put into a cylinder of water a centimeter and covered with enough water to make with it a thin paste. A rapid stream of nitrous fumes are passed through it, until the toluidine salt goes into solution completely, and for some time afterward. The cylinder is kept in an ice-bath during the operation. If the temperature is not kept down, immediate decomposition of the nitroso compound takes place. The reaction is complete when a sample of the mixture gives a deep blue with dilute sulfuric acid and ferrous sulfate.

The diazotic solution of toluene-para-diazo nitrate is then poured into a beaker surrounded with a freezing-mixture, and an equal bulk of strong alcohol added. The cyanide is then added, the whole mixture stirred constantly, and the potassium cuprous cyanide solution added. The mixture becomes a cloudy appearance which does not disappear on further stirring. In a few moments the precipitation

added, stirring as before, until further addition of ether does not precipitate any more of the diazo-compound. The nitrate should not be filtered off at once, as it is

washed without trouble. It is first drained of the mother-liquor upon the filter-pump, then washed two or three times with a small quantity of absolute alcohol, and then with ether until the washings are colorless. When drained completely it is placed on a dry-

longer perceptible.

The para-diazo-

is of a light yellow color. The crystals are very minute

possible, when made in quantity, to prevent its turning slightly yellow before it can dry. The pure dry salt does not change color rapidly.

Unless great care is taken in the preparation of the nitrate, it [illegible] and [illegible], which cannot be removed with [illegible].

The yield of the nitrate is fair, being generally somewhat more than the weight of the tolidine used.

Preparation of Para-Diazo-Toluene Sulphate.

The sulphate is more easily made than the nitrate. The method used was that described by Nevile[1]. 20 grams of the tolidine are dissolved in the [illegible] and [illegible] c.c. of water added. When the tolidine is dissolved, 30 grams of pure sulphuric acid are added, drop by drop, with constant shaking. The

[1] Dissertation, 1887.

flask is then placed in ice water and nitrous fumes passed through for an hour or more. The reaction is [illegible] when a drop of the solution of the diazo-compound does not smell of toluidine. The solution of the diazo-compound does not crystallize so readily as in the case of the nitrate. The crystals of the diazo-sulphate are heavier than those of the toluidine salt, and have a slightly different appearance.

The contents of the flask are poured into cold ether. Most of the diazo-compound separates out at once; but on standing the separation is more complete, and the diazo-compound becomes crystalline and easier to wash. After an hour or two the diazo-compound is filtered off and washed with a small quantity of absolute alcohol, and then with ether.

The para-diazo-toluene sulphate, as thus obtained, is a beautiful white salt of most attractive appearance. It is much more stable than the nitrate. The yield is very good, being [illegible]

within a very few grams of the theoretical yield

Decomposition of Ethyl Nitrate with the Production of Nitric Oxide at the Ordinary Atmospheric Pressure.

40 grams of ethyl nitrate were placed in a long necked flask of 1 liter capacity, and covered with 100 c.c. absolute methyl alcohol (from sodium); the flask was then placed in a water bath and provided with a return condenser. The decomposition began at the room temperature but was very slow. On heating the bath to 50-60° C. the decomposition went on quicker and regularly. A slow current of nitrogen gas was passed through the alcohol and heated for a short time to ensure complete decomposition. In this way 133 grams of the nitrate were decomposed with about 450 c.c. absolute methyl alcohol.

The different portions were combined and the alcohol distilled off. The alcoholic distillate was poured into about five times its bulk of concentrated solution of sodium chloride. A yellow oil rose to the surface and was separated. The residue in the flask was made alkaline and distilled with steam from a Sorbier generator, yielding an aromatic oil. This was treated with ether from the alcoholic distillate, washed with caustic soda, then several times with water, dried with calcium chloride, and fractioned. A few drops came over between 170° and 180°. The main portion at 175–177° and about 2 c.c. above 180°.

The lower boiling portion was also fractioned by treatment with fuming nitric acid and a liquid was obtained which smelled like nitro-benzene. This was reduced in a test-tube with tin and hydrochloric acid, the whole made alkaline and distilled with steam, and the aniline [illegible]

smelled like para-toluidine, but the quantity was too small for satisfactory testing.

The fraction boiling between 172° and 177° was redistilled several times, when it boiled at 174.5° (cor.). 1.5 grams; a colorless mobile oil of pleasant odor. Its boiling point corresponds to that of the methyl ether of para-cresol (174°-175°) described by Körner.[1]

To test further its identity, 2 grams of the oil were oxidized with potassium permanganate in alkaline solution, and an acid obtained which melted at 184°. This agrees fairly well with the melting point given for anisic acid (180°). The oil is therefore the methyl ether of para-cresol, $CH_3.C_6H_4.OCH_3$ (p).

The fraction of the oil which came over above 177° was found not to have any definite boiling point, and was probably a complex mixture. Nothing was obtained from it.

The residue in the steam flask was acidified with sulphuric acid and again distilled

[1] Zt. f. Ch. 1865, p. 326.

with steam. Nothing came over except water.

The contents of the steam flask were poured out and the liquid evaporated. Nothing was found but sodium sulphate. The tar — a black, solid mass — was extracted with ligroïn (b.p. 90°), after which the insoluble had been dried, and three grams of a yellow solid obtained which on recrystallization several times from ligroïn and alcohol, melted at 80°.5 (cor.). The crystals obtained from ligroïn were long, flat needles with serrated edges. These were not brittle, and were consequently difficult to powder. The crystals obtained from alcohol were fine, short needles which were quite brittle.

The melting point and other physical properties of this substance made it probable that it was identical with the dinitro-para-cresol (m.p. 85°) obtained by Fittig[1] by the action of nitric acid upon the ortho-para-cresol. To prove its identity, the potassium salt was made, from it the silver salt, and from this, by treatment with ethyl iodide the ethyl ether. This melted

[1] Ann. 217, 163.

agreed with the description given by Städel of the ethyl ether of para-cresol. The melting point found was 71; that given by Städel is 75°. The relative difference between the melting points of the dinitro-cresol and its ethyl ether is practically the same. I judge, therefore, that the difference is due to the thermometers. The thermometer used throughout this investigation was carefully compared with a standard thermometer for temperatures between 14° and 92° C. Temperatures near 183° were corrected by the boiling point of naphtalin.

The melting point of dinitro-para-cresol ($CH_3, NO_2, OH, NO_2 = 1, 3, 4, 5$) is given by different investigators variously as 79°–80°,[1] 82°,[2] 83°,[3] 83.5°,[4] 84°,[5] 85.°[6] In order to obtain the melting point with greater certainty, a quantity of dinitro-cresol was prepared. 36 grams of para-cresol were made, and diluted with 36 grams of glacial acetic acid. 54 grams nitric acid (sp. gr. 1.4) were diluted with 108 grams glacial acetic acid.

[1] Ber. 13, 1946. [2] Ber. 6, 974. [3] Ber. 7, 1023; 14, 1568. [4] Ber. 7, 536.
[5] Ber. 2, 207; 8, 685; 14, 986; Ann. 173, 201. [6] Jahresb. 1866, p. 360.

The two solutions were dropped slowly from dropping funnels into a flask surrounded by a freezing mixture. After several hours the mixture was warmed on the water-bath, and poured into much cold water. A yellow solid was obtained. [illegible] The crude product, which was wholly dinitro-para-cresol, was recrystallized from alcohol until repeated recrystallizations failed to cause any change in the melting point. The melting point of the dinitro-para-cresol was found to be constant at 80.5° (cor.).

Action of Nitric Acid on Para-Tolyl-Urethane.

[illegible] Under certain conditions dinitro-para-cresol is obtained by the action of nitric acid, it was found

[illegible] of interest.

[illegible] nitric acid (60% 1.7) [illegible] with [illegible] acid. [illegible] low [illegible] with a [illegible] with ice, and allowed to stand over night. In the morning the solution was [illegible] water, and the whole allowed to stand. The next day the water had cleared up, and at the bottom was [illegible] crystals. These were separated from the oil by the filter-bump and re-crystallized from alcohol. [illegible] This proved [illegible] to be identical in every respect with the identity of this substance the ethyl ether was made as before. It melted at 71°.

The quantity of oil from which the crystals were separated was so small that nothing more

from a dropping funnel on to 40 grams of pure concentrated nitric acid, in a flask provided with a return condenser. Heat was applied to start the reaction. [illegible] After about half the ether had been added 20 grams of fuming nitric acid were added, and the rest of the ether was run in. 10 grams of concentrated nitric acid and 20 grams of concentrated sulphuric acid were then added, and the mixture boiled until [illegible]. The flask was then poured into cold water, and after a time the oil which first separated out became crystalline. The crystals were separated from the oil by the filter pump and recrystallized from alcohol. They melted at 12[illegible]. The crystals were slightly yellowish color. They looked like the ethyl ether

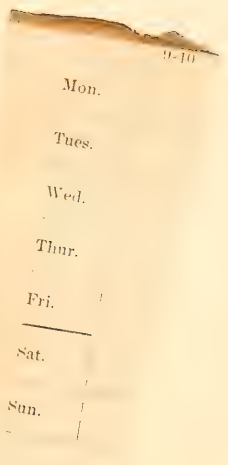
of dinitro-para-cresol. The melting point showed [illegible].

The yield was very small, only 0.2 gram of the purified substance. Most of the ether had been oxidized completely by the strong nitric acid.

The action of dilute nitric acid upon para-methoxy-toluene is thus not only to introduce two nitro groups, but also to saponify the ether. This is what one would expect from the work of Städel. From para-cresol ethyl ether he obtained dinitro-para-cresol and dinitro-para-cresol [illegible] from ortho-cresol ethyl ether he obtained exclusively dinitro-ortho-cresol,[2] and from para-cresol [illegible] the dinitro-para-cresol.[3]

The action of dilute nitric acid is somewhat as follows: Saponification does not [illegible] from such mild treatment. Some of the dinitro-cresol ether [illegible] with concentrated nitric acid [illegible]

[1] Ann. 217, 161. [2] Ibid. 217, 168. [3] Ibid. 217, 180.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without any effect whatever. It is probable that when the nitro groups are entering, the equilibrium of the molecule is so disturbed that saponification is effected by influences which do not ordinarily [illegible].

Another experiment was made with 20 grams of para-diazo-toluene nitrate, in the hope of determining more accurately the character of the reaction with methyl alcohol, both as to the yield of ether and also as to the other substances formed. [illegible] carried on as above described. The oil separated into three fractions: one, about 1 c.c., boiling at 100°-130°; the main portion, about 40 grams, boiling at 173°-177°; [illegible] about 2 c.c., boiling at 215°-225°. There was some tar left in the distilling [illegible].

The fraction boiling at 100°-130° was [illegible] nitric and sulphuric acids [illegible]

cased, and then the whole was poured upon ice. A white solid separated out, which was recrystallized from alcohol, and found to melt at 70.5°. This is ordinary dinitro-toluene (2, 4), and proves the presence, to some extent, of the diazo compound.

The fraction boiling at 215°-225° only 2 c.c.) was oxidized with potassium permanganate, in the hope that a crystalline substance would be obtained which would identify it. A few white crystals (probably something like urea, were obtained, which melted at 181°(cor), but the quantity was too small to permit an analysis.

The tarry residue in the steam flask was extracted with ligroin as before, and 5.5 grams of dinitro-para-cresol obtained melting at 85°. The residues and distillates were thoroughly worked over, but nothing further was found in them.

The main product of the reaction between

methyl alcohol and para-diazo-toluene nitrate at the ordinary atmospheric pressure is para-methoxy-toluene. A very small quantity of toluene is also formed. A little dinitro-para-cresol is formed, due probably to the action of the nitric acid liberated in the reaction. The reaction thus consists mainly in the substitution of the methoxy- for the diazo-group:

$$CH_3.C_6H_4.N_2NO_3 + CH_3OH = CH_3.C_6H_4.OCH_3 + HNO_3 + N_2.$$

The presence of the toluene is accounted for by the equation:

$$CH_3.C_6H_4.N_2NO_3 + CH_3OH = CH_3.C_6H_5 + CH_2O + HNO_3 + N_2.$$

[illegible] no trace of formaldehyde [illegible] observed during the decomposition, [illegible] no indication [illegible] presence [illegible] as one of the products of decomposition.

Decomposition of Para-Diazo-Toluene sulphate with methyl alcohol at the ordinary temperature.

47 grams para-diazo-toluene sulphate were placed in a flask provided with a return condenser, together with 200 c.c. absolute methyl alcohol, and the flask placed in a water-bath. The decomposition did not begin until the boiling-point of the mixture was reached. The evolution of nitrogen went on quietly and steadily, and in about half an hour the decomposition was complete.

Fifty grams of the sulphate were decomposed in the same way, with 250 c.c. absolute methyl alcohol.

The two portions were united and the alcohol distilled off. The distillate was diluted with water, and a yellow oil separated. The distillation was then continued with steam, and the oil which came over separated and united with that from the electrolytic distillate. The yield of crude oil was

40 grams. On fractioning, almost all of the oil came over at 170°-180°, and, on redistilling, from 174°-176° (corr). This is again the methyl ether of para-cresol.

A few drops of oil distilled over below 170°; when redistilled, five or six drops came over between 100° and 130°. These were treated with strong nitric [illegible] and a little water, [illegible] a quantity of tarry [illegible].

A small quantity of oil distilled above 180°, and an [illegible] was made to get [illegible].

The quantity of tar left in the steam flask was very small, compared with that obtained in the decomposition of the diazo-nitrate.

Part of the liquid in the steam flask was neutralized with barium carbonate and filtered. Addition of sulphuric acid to the filtrate [illegible]

a slight cloudiness, probably due to the presence

of [illegible] of formed [illegible] by the

steam.

The reaction with the diazo-sulphate is again the methoxy reaction, almost exclusively. The reaction is much cleaner than is the case with the nitrate, and the yield of methoxy-toluene is [illegible].

Decomposition of the Diazo-Toluene Nitrate with Methyl Alcohol under Diminished Pressure.

In the experiment 41 grams of the diazo-toluene nitrate were decomposed with 120 c.c. absolute methyl alcohol. The flask was connected to a return condenser, the other end of which was connected to a suction bottle and a water-pump. During the

experiment the [illegible] at 490-500 mm. Slight signs of decomposition were observed at the ordinary temperature. At 40° the [illegible] steadily. The [illegible] were passed through water, and the water tested for an aldehyde with ammoniacal silver nitrate, but no indication of an aldehyde was found.

The products were studied as before described, first traces of the nitrite, then making [illegible] with cuprous chloride and [illegible]. The [illegible] which came over was separated when [illegible], into two fractions, one boiling at 105°-112° and the other at 172°-177°, showing that here again toluene and [illegible] were the products of decomposition. The yield was better than in the experiment with the [illegible] at ordinary pressure — 6 cc. of ether and 2 of toluene. There was a small quantity of oil left in the distilling bulb at 180°, which proved to contain toluidine which had not been diazotized.

When the distillate from the steam flask came over clear, the contents of the steam flask were acidified and steam again passed through. About 2 c.c. of a dark [illegible] in a freezing mixture. The mass was put on a dry [illegible] On cooling the alcohol they reappeared and were separated and dried; melting point, 32°. The substance formed [illegible] with steam, its [illegible] red. It was very soluble in alcohol, and was volatile with boiling alcohol. These properties show that it is the mono-nitro derivative of para-cresol. (1, 3, 4.)

The differences noted between the reaction [illegible] The one at ordinary pressure were such as were to be expected. The reaction was cleaner than the one at ordinary pressure, probably due to the lower temperature; and the nitro-compound formed did not contain two nitro groups. It is to be noted also

that the decomposition of toluene sulphonic acid in reaction at ordinary pressure.

Decomposition of Para-Diazo-Toluene Sulphonate with Methyl Alcohol under Diminished Pressure.

Using the same method as in the preceding experiment, 5·7 grams of para-diazo-toluene sulphonate were decomposed with 25·0 c.c. absolute methyl alcohol, with a diminution from the ordinary pressure of 500 m.m. The decomposition took place slowly when the alcohol was heated up to its boiling point, and was complete in about four hours. The residue was distilled with steam, the steam distilled over first and the oil from the two portions united. The yield of crude oil was 2·5 grams. On fractioning, a few drops came over between 100° and 120°, consisting chiefly of toluene. Almost the whole of the oil passed over between 170° and 177°.

The reaction in this case is a very clean one. The [illegible] toluene [illegible] trace of toluene.

Decomposition of Para-Toluene-Sulfonic with Water Vapor under Increased Pressure.

[illegible] was placed in a [illegible] flask and covered with wire netting. The flask was fitted with a two-holed rubber stopper, and connection made with a safety-valve and a manometer. By changing the weight on the safety-valve the pressure could be kept at any desired point.

[illegible] with [illegible] c.c. [illegible] with an inverse [illegible] 5 [illegible] mm [illegible] The decomposition [illegible]

[illegible] about 15°.

After the [illegible] the [illegible] of oil [illegible] of oil accumulated out. The contents of the flask were then [illegible] distilled with steam. [illegible] an orange-colored solid appeared in the condenser. The quantity of this was very small. The distillation with steam was continued [illegible] the distillate [illegible] the oil [illegible] in the ether. The ether was evaporated. The [illegible] in the ether [illegible] in the oil.

On fractioning the oil no trace of toluene was found. Most of the oil, — 12 grams — passed over between 172° and 177°. A small quantity was lost in the distillation of [illegible]

180°. This was poured into a small beaker and cooled in a freezing mixture, when crystals appeared in it. These were filtered off and recrystallized from alcohol. They melted at 113°, and had the other properties of mononitro-toluidine. Their formation here was due to the action of the nitric acid [illegible] toluidine. [illegible] red solid which distilled from the alkaline solution.

[illegible] solution was recrystallized from alcohol and found to melt at 32°. It was identical with the mononitro-cresol obtained when working at reduced pressure.

The [illegible] 1.1 grams. Nothing crystallized [illegible] extracted from the tar.

The occurrence of mononitro-cresol instead of dinitro-cresol in this experiment is due, probably, to the fact that the alcohol was distilled off under reduced pressure, and the action of the nitric acid on the cresol ether was therefore not so energetic as when the alcohol

was boiled off at a higher temperature.

Decomposition of Para-Diazo-Toluene Sulphate

[illegible]

In this experiment 60 [illegible] para-diazo-toluene sulphate was suspended in 250 c.c. absolute methyl alcohol under an increase of 50-60 [illegible] pressure in a rotating autoclave. The decomposition began at about 60°. [illegible] passed through the residue, exactly as in the case of the nitrate, except that the contents of the flask were not made alkaline. Yield of crude oil, 25 grams. On fractioning, [illegible] 170, [illegible] to be toluene by making the dinitro-derivative and testing the melting point. Almost all of the oil distilled at 172°-177°. About 1 c.c. of dark red oil remained above 180°. This would not crystallize, and

nothing was done with it. There was less tar formed in this reaction than in any other so far performed.

The reason the reaction is so smooth, the quantity was.

Decomposition of Para-Diazo-Toluene Nitrate with Cuprous Nitrate.

The work of Beeson[1] on the action of diazo-benzene nitrate and sulphate with cuprous sulphate, and with methyl alcohol in the presence of caustic potash or zinc dust, made it probable that para-diazo-toluene nitrate and sulphate would give the hydrogen reaction in the presence of these and similar substances.

44 grams of para-diazo-toluene nitrate were added gradually to 200 c.c. methyl alcohol in which

[1] Dissertation, 1893; Am. Ch. Jr. 16, 244.

15 grams of [illegible] were distilled. The [illegible]
[illegible] with [illegible]
nitrate. [illegible] in the [illegible] the
experiment. The products of the decomposition were
distilled with steam. 9 grams of crude oil were
obtained. [illegible] to be [illegible],
[illegible] and a [illegible] was obtained in the distillate
[illegible] 120°. This was probably the [illegible]
[illegible] to the [illegible] and [illegible] in the
[illegible]. There was a considerable quantity of tarry
[illegible] left in the steam flask. [illegible]
[illegible] [illegible] [illegible] through it but no attempt
to [illegible] the [illegible] were [illegible].

In this case as in the [illegible] by [illegible]
by [illegible] the hydrogen [illegible] is the one
which [illegible].

[illegible] with Sodium Methylate.

52 grams of para-diazo-toluene sulphate were decomposed with 200 c.c. methyl alcohol in which 12 grams of sodium had been dissolved. The method of procedure was the same as in the case of the nitrate. The yield of tar was small — 7.5 grams. On distilling, practically all of it came over at 109° to 111°. The main product of the reaction was tar, from which nothing could be obtained. This was to be expected for reasons [illegible] but from the reaction between sodium methylate and diazo-benzene sulphate.

The reaction in this case, as with the nitrate is the hydrogen reaction exclusively.

Decomposition of Diazo-Diazo-amino Nitrate with Ethyl Alcohol and the Ether.

75 [illegible] 40° [illegible] 25° [illegible]. The diazo compound was added very slowly and in small portions, shaking the flask after each addition. Decomposition took place immediately, but at first the action was very slow. Soon, however, enough heat was furnished by the reaction to make it necessary to moderate the action by cooling the flask. The whole was let stand over night, and the next day it was boiled for a short time on the water-bath, to insure complete decomposition. The alcohol was boiled off, and the residue distilled with steam. By far the greater part of the oil came over with the alcohol. Yield of crude oil, 11 grams. Practically the whole of this came over between 107° and

114°, and all but a few drops at 109°. [illegible]

[illegible] oil remained in the bulb. [illegible]
[illegible] left in the steam flask was considerable.

The reaction is here, as was expected, [illegible]
[illegible] reaction.

[illegible] Para-Diazo- [illegible]
[illegible] and Caustic Potash.

[illegible] 21.4 g. [illegible]
sulphate were decomposed with 200 cc. methyl alcohol
and 25 g. [illegible] caustic potash. [illegible]
1 [illegible]. This distillate [illegible], 10°. [illegible]
[illegible] with the tar.

Here, as above, the hydrogen reaction above takes
place.

[illegible] experiment [illegible] in which
heat was applied. The decomposition took place very

rabidity, and the products of the reaction were, besides tar, toluene and methoxy-toluene in about equal quantities. This would tend to confirm the idea that heat is favorable to the alkoxy reaction.

Decomposition of para-Diazo-Toluene Nitrate with Methyl Alcohol and Potassium Carbonate.

In exactly the same way as before, 37 grams para-diazo-toluene nitrate were decomposed with 150 c.c. methyl alcohol and 40 grams anhydrous potassium carbonate. The decomposition took place without the aid of heat. The alcohol was boiled off and steam passed through the residue. When the distillation with steam was nearly ended, a very little reddish oil containing crystals appeared in the condenser. The quantity was so small that nothing could be done with it. 11 grams of crude oil were obtained, which

[illegible] 17.

The effect of an alkaline carbonate upon the [illegible] the reaction is, thus, the same as that [illegible].

[illegible] with Methyl Alcohol and Potassium Carbonate.

4. [illegible] were decomposed with 200 c.c. methyl alcohol and 40 [illegible] potassium carbonate. The method was the same as above given. Yield of crude oil, [illegible]. The [illegible].

Decomposition of Para-[illegible] by Zinc Dust.

Besson[1] obtained benzene and diphenyl by heating [illegible] with zinc dust. The following experiments were made, to see whether the corresponding products would be formed in the case of [illegible] with zinc dust.

A [illegible] was heated to 180° C. until it would [illegible] with zinc dust. The reaction took place at once, and was moderated by putting the flask into ice water. The products were treated with steam in the usual manner. [illegible] passed over. This proved to be toluene.

The [illegible] was heated in the oil bath to 300° after the oil had all distilled over. The residue was extracted with ether, in the hope that it would

[1] Comptes Rendus, 1893; Am. Ch. Jr. 16

weight is obtained. On boiling off the ether, about 5 grams of a clear, yellowish, gummy substance were obtained, which was probably a camphor, nitrate. All efforts to separate something which [illegible].

Decomposition of [illegible] with Methyl Alcohol and Zinc Dust.

Exactly as in the preceding experiment, 38 grams [illegible] were treated with 100 c.c. methyl alcohol and an excess of zinc dust. The oily [illegible] was treated, and the yield [illegible] in the preceding experiment.

During the course of this experiment it was noticed that when fresh zinc dust was added to the mixture of zinc dust, methyl alcohol and diazo-compound, there was immediately a more rapid evolution of nitrogen, although an excess of zinc dust was already

present. It was thought that perhaps this might be due to the more energetic action of the zinc oxide, which is always present in small quantity in zinc dust. To test the influence of an oxide upon the course of the reaction, experiments were made with the diazo-nitrate and sulphate with methyl alcohol in the presence of zinc oxide.

Decomposition of Para-Diazo-Toluene Nitrate with Methyl Alcohol and Zinc Oxide.

44 grams of para-diazo-toluene nitrate were added gradually to 200 c.c. methyl alcohol and 20 grams powdered zinc oxide. No decomposition took place at the room temperature. The flask was placed on a water-bath, provided with a return condenser, and heated slowly. The decomposition began at about 40°, and went on quietly and slowly, as when

alcohol alone was used. After some time, however, the action had to be kept back by taking the flask out of the bath. The volatile products of the decomposition were separated in the usual way. The yield of crude oil was 15 grams. On fractioning, this was found to consist of about equal parts of toluene and methoxy-toluene. The residue in the steam flask was unbrominable and nothing was done with it.

Decomposition of Para-Diazo-Toluene Sulphate with Methyl Alcohol and Zinc Oxide.

54 grams of para-diazo-toluene sulphate were [illegible], with 250 c.c. methyl alcohol and 20 grams powdered zinc oxide. The decomposition phenomena were similar to those in the case of the nitrate. After the decomposition had well begun, the mixture thickened up, and

became quite frothy, and the bubbles of escaping nitrogen caused it to swell up so as nearly to fill the flask. After a time the mass became [illegible]

[illegible]

[illegible]

[

[illegible] reactions.

The quantities obtained in the above-described reactions are significant only in a general way; still, it is of interest to compare them, so far as the data will allow. The percentage of the theoretical yield is given:

	Para-methoxy-toluene.	Toluene.
Nitrate with alcohol, ord. pr.,	29	trace.
Sulphate " " " "	66	trace.
Nitrate " dil. "	22	10
Sulphate " " "	77	Trace
Nitrate " conc. "	39	—
Sulphate " " "	61	trace.
Nitrate " sodium methylate,	—	36.
Sulphate " " "	—	32.
Nitrate " picric and K.H,	—	74.
Sulphate " " " "	—	69.
Nitrate " H_2CO_3,	—	53.

Sulphate with alcohol and K_2CO_3,	——	——	44.
Nitrate " " " Zn,	——	——	—x
[illegible] " " " "	——		46.
Nitrate " " " ZnO,	17	——	22.
[illegible] " " " "	20		48.

There may have been, [illegible] traces of methoxy-toluene in three cases in which toluene was the main product formed; but no method is suggested itself for detecting traces. The methoxy-toluene in mixtures, no proof of its presence was found.

[illegible]

Summary of Results.

Several conclusions seem to be justified by the results of the experiments recorded in this paper.

The suggestion of Remsen and Dashiell,[1] that lowering of temperature and pressure tends to favor the hydrogen reaction, finds support in the reaction of the nitrate, which at diminished pressure. The sulphate, too, gives a better yield at lower temperature than the nitrate, but it decomposes at a lower temperature. But the sulphate gives a better yield [illegible] at the pressure decreases. The largest percentage of [illegible] is given by the sulphate under reduced pressure.

The action of dilute nitric acid upon [illegible],

[1] Am. Ch. J. 15, 124.

makes it probable that in the reaction nitro-phenols are formed by the reaction of diazo-nitrates with acetic acid, these products are formed by saponification of the ethereal compound, the introduction of nitro-groups taking place at the same time.

The fact that the diazo-salts do not decompose rapidly at a low temperature in the presence of caustic potash, was made use of and mentioned. It may also be of importance in the formation of iso-diazo-compounds similar to those studied by Bamberger.[1]

The results obtained by Beeson,[2] by the use of alkalies and zinc dust, were found to hold good in the same manner, with the exception that no di-tolyl was found. One substance which will materially aid liberated in the decomposition of the dia-

[1] Ber. 27, 679.

[2]

compound will probably determine the hydrogen reaction, at least to some extent. This may be due to the fact that the reaction takes place at a lower temperature. When zinc oxide was used the temperature at which decomposition took place was higher than in the other case in which neutralizing agents were used, and the products were mixed and the reaction taking place in both ways. Why zinc should be more effective than zinc oxide, it is hard to say. Equations can be written which account for all the substances found, but they are of little value in the present state of knowledge.

$2\,CH_3.C_6H_4.N_2.NO_3 + Zn + CH_3OH = 2\,CH_3.C_6H_5 + Zn(NO_3)_2 + CH_2O.$

$CH_3.C_6H_4.N_2SO_4H + Zn + CH_3OH = CH_3.C_6H_5 + ZnSO_4 + CH_3OH.$

$CH_3.C_6H_4.N_2SO_4H + ZnO + CH_3OH = CH_3.C_6H_5 + ZnSO_4 + CH_2O + H_2O.$

$2\,CH_3.C_6H_4.N_2NO_3 + ZnO + 2\,CH_3OH = 2\,CH_3.C_6H_5 + Zn(NO_3)_2 + 2\,CH_2O + H_2O.$

Attempts were made to get benzoic, [illegible] but without success.

Biographical Sketch.

The earlier [illegible] was received [illegible]
[illegible] was born [illegible]
[illegible], on [illegible]. He entered [illegible] at [illegible]
Ohio. His college course was pursued at Oberlin College.
He was graduated in 1857 with the degree of A.B. The
[illegible] years following he spent in the study of theology
[illegible]. The next four years were spent in the study of chemistry, one at Oberlin, and three at the Johns Hopkins
University.

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